MARKES
international

Technical Support

Released: April 2014

Application Note 026

Minimising analytical interference from water during the analysis of sorbent tubes

Approaches to eliminating water interference

There are four basic approaches to eliminating interference from water when monitoring air using sorbent tubes:

1. Minimising the volume of air sampled

This approach is effective, but may be limited by monitoring constraints such as detection limits, minimum pump flow rates, and the need to collect ‘time-weighted-average’ concentration data over a specified time.

2. Selection of hydrophobic sorbents in the sampling tube

It is possible to minimise water collection by selecting, where possible, a hydrophobic sorbent for the sample tube (see Application Note 005). This can be done for compounds with boiling points equal to or greater than n-C_5. True hydrophobic adsorbents, such as Tenax® TA and Carbograph™ 1TD, have such low affinity for water that a ‘steady state’ is quickly reached during sampling, whereby water elutes from the far end of the tube as fast as it is being pumped onto the sampling end.

If Tenax TA, Carbograph 1TD or any other hydrophobic sorbent offers quantitative retention of all the target analytes, no other water management steps will be required during the analysis, even when monitoring high-humidity atmospheres (>90% relative humidity).

N.B. It is essential that tubes are at the same temperature as the air or gas being sampled at the start of sampling. Otherwise, moisture will condense on the (relatively) cool tubes.

When monitoring a range of analytes that includes compounds more volatile than n-C_5, stronger, less hydrophobic sorbents are required in the sample tube. These should generally be used behind a bed of medium and/or weak sorbent to prevent high-boiling compounds reaching the strong sorbent and adsorbing irreversibly. Water retention in these tubes may be minimised by using a bed of the stronger, less hydrophobic sorbent that is as short as possible.

Glass tubes, which have a narrower i.d. (4 mm) than the 5 mm i.d stainless steel tubes, also help reduce water retention. Their smaller internal diameter means that the mass of sorbent for a given bed length is lower than in their stainless steel counterparts.

3. Sample splitting

If the concentration of target analytes is relatively high (5 ppb or above), it is usually possible to eliminate sufficient water to prevent analytical interference by using sample splitting – even when less hydrophobic sorbents are used. Markes’ thermal desorbers offer three splitting options:

(a) Between the sorbent tube and the focusing (‘cold’) trap during primary (tube) desorption

(b) Between the focusing trap and the capillary column during secondary (trap) desorption

(c) Both of the above (known as double splitting).

In atmospheres with VOC concentrations above 10 ppb, when large-volume air samples have been collected, or when sensitive detectors are in use, it may be necessary to split the sample to prevent overloading the analytical column or detector. As with the selection of hydrophobic sorbents, the selection of a significant overall split ratio (>20:1) should mean that no further water management steps will be required.

4. Selective elimination of water

The fourth approach to water management, required when monitoring trace-level, very volatile analytes in humid atmospheres with less hydrophobic sorbents, is selective purging of water from the tube (and/or focusing trap) and from the analytical system before analysis.

Modern strong sorbents, such as carbonised molecular sieves, are already much less water-retentive than pure molecular sieves or charcoal. However, some water will be retained by a tube whenever strong sorbents are used. This residual water can be eliminated from tubes by ‘dry-purging’ them with a known volume of pure dry gas in the sampling direction, before desorption.

During this process, care must be taken to ensure safe sampling volumes are not exceeded for the most volatile target analytes, *i.e.* that volatile target analytes are not swept to vent along with the excess water.

Markes’ TC-20™ multi-tube conditioner is a convenient device for dry-purging up to 20 tubes in parallel.

The UNITY™ and automated TD-100™ thermal desorption systems from Markes also offer dry-purge accessories for automatic dry-purging of every tube with carrier gas, at ambient temperature, before analysis. This dry-purge step is carried out with gas flowing in the sampling direction, *i.e.* opposite to the desorption direction.

A significant percentage of retained water can also be eliminated by using a similar dry-purge process for the focusing trap during the primary (tube) desorption stage of analysis. One of the trapping options available for Markes' TD systems is a water management trap). This contains four separate beds of sorbent, including an initial plug of glass or quartz wool, in a total bed length of 60 mm. When maintained at 30°C, this focusing trap is able to selectively retain any analyte that can be quantitatively retained on a sorbent tube at ambient temperature, while allowing selective elimination of water. If this trap is used in conjunction with an extended tube desorption time, water will be selectively eliminated from the focusing trap before it heats, initiating the GC run. Safe sampling volumes for target analytes are unlikely to be exceeded for the focusing trap, as total purge and desorption gas volumes are invariably much lower than initial tube sampling volumes.

In cases where extremely humid vapours are to be monitored, it is wise to both dry-purge the tubes before analysis and to use a trapping temperature of 30°C in the internal focusing trap to allow dry-purging at this stage too.

Conclusions

Using one or more of these four approaches to water management, it is possible to eliminate sufficient water to prevent analytical interference with even the most water-sensitive GC detectors and columns[1].

References

1. More information on water management for capillary GC analysis of volatile organics in air can be found in: D. Helmig and L. Vierling, Water adsorption capacity of the solid adsorbents Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Carbosieve SIII and Carboxen 569 and water management techniques for the atmospheric sampling of volatile organic trace gases, *Analytical Chemistry*, 1995, 67: 4380–4386.

Trademarks

TC-20™, TD-100™ and UNITY™ are trademarks of Markes International.

Carbograph™ is a trademark of LARA s.r.l., Italy.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.